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Method to the production of cellulosischen shaped bodies with high adsorption capacities

1 The invention relates to a method to the production of shaped bodies with high adsorption capacities in the drying wet extruding procedure by forming a solution from 5 to 20 mass % cellulose in an aqueous tertiary amine oxide, extrusion of the solution, forgave the extrudate in not precipitating Mediums and failures of the shaped bodies in an aqueous drop bath. The invention relates to also a composite out after the invention process manufactured shaped bodies, in particular fibers, and its use as filter material.

It is known, cellulosische shaped bodies, to manufacture in particular fibers and foils by a solution of cellulose in amine oxide hydrate, preferably in N-methylmorpholine-N-OXIDE-monohydrate deformed and with a nonsolvent for the cellulose, preferably waters, one coagulates.

3 By different moulding and simultaneous orientation of the cellulose molecules one receives products with various applicability in textile and technical operational areas.

In EP 0,789,790 is the production of shaped bodies with anion exchange characteristics after the amine oxide method described. These exchange characteristics become achieved by the fact that the cellulose contains 0.02 to 30 mass % a Polyalkylenimins. These shaped bodies have only a small basicity and the adsorption capacity are on anions limited.

5 By the limited receptiveness of the Spinnlösung for the Polyethyleniminderivat soluble in the solution the formed shaped bodies also only a corresponding limited exchange capacity has.

From WHERE 95/35044 a cigarette filter from a fibrous composite material with Lyocell Stapelfasern is known. This filter serves for the removal of tar and solid particle from smoking Rome. The filter material contains no groups, which are capable to the adsorption of ions or polar molecules.

The invention is the basis the object to create a method to the production electric molecules or ions loaded by cellulosischen shaped bodies
7 with high adsorption capacities opposite polar or. The other a method is to become the production of shaped bodies, in particular fibers and foils provided, which are suitable due to their high adsorption capacity to the production filter material. Finally also a composite is to become from these shaped bodies provided, which is more insertable as filter material in cigarettes, household machines and in other ranges of applications. Other advantages result from the ensuing description.

This object becomes with that initially mentioned methods according to invention by the fact dissolved that one extrudes a solution with 0,01 to 300 mass %, related to cellulose, at least an ion exchanger of a Kongrösse of, 100 pm. Surprisingly it was found that the ion exchanger incorporated in the manufactured shaped bodies for out wäss the rigen solutions, gases or steam to adsorbent ions and/or polar molecules very good accessible are, although the imbedding of active substances in Matrices accompanies generally with an activity reduction of these substances. Beyond that found could become that manufactured the according to invention shaped bodies show a significant higher adsorption speed than the same ion exchangers in the conventional Perl form. The adsorption capacity is dependent of the content of the incorporated quantities of the ion exchanger physical into the cellulose matrix. For example have the shaped body according to invention, existing from same parts by weight cellulose and ion exchanger an adsorption capacity, which is more comparable with the commercial ion exchanger in Perl form with approximately 50% water content.

After the preferable embodiment of the invention process contains to the extrusion used the solution 1 to 200 mass %, preferably 10 to 150
9 mass %, related to cellulose, the ion exchanger. Particularly prefered becomes solutions, which contain 70 to 100 mass % ion exchangers related to cellulose.

Preferably the grain size of the ion exchangers lies in the range 4 25, over, in particular in the range < 15 pm. Commercial ion exchangers used can become, whose grain size lies however the generally far range according to invention above. The grain size achieved one by the Aufmahlung of the commercial, z, required for the incorporation into the solution. B. perlförmigen ion exchanger. One appropriately adjusts the grain size of the ion exchangers by grinding and sifting in a fluidized bed against jet mill with Turboplex Feinsichtung.

11 Prefered ones have the ion exchangers one polystyrene or Polyacrylatharzbasis. In particular the resins of acidic or basic derivatized styrene Divinylbenzol-copolymer resins or acrylic acid Divinylbenzol-copolymer can be resins. In principle also different carrier materials can come for the exchange's groups to the use, like z. B. Cellulose.

& top The formation, of the extrudable solution loaded with the ion exchanger can take place in various embodiments. With a Ausfüh rungsform dispersed one the ion exchanger in the already formed cellulose solution. With an other Ausführungsfonn one forms first a mixture from cellulose, amine oxide and water, manufactures a suspension of the ion exchanger in waters and adds the suspension of the mixture mentioned and transfered these by Abdestillieren of water into the cellulose solution. This method has the advantage that the formation of the suspension of the finely divided ion exchanger is in the water light possible as the dispersion in the formed cellulose solution. If necessary suspending in waters can become by addition of a surfactant supported.

13 With a third embodiment suspended one the cellulose and the ion exchanger in a mixture from amine oxide and water and forms then from the suspension by water evaporation up to the mono hydrate stage the solution of the cellulose. In all three cases the ion exchanger can cover several various ion exchangers, in particular at least an anion exchanger and at least a cation exchanger. The ion exchanger is in the cellulose solution insoluble and becomes with the precipitation of the cellulose into these incorporated, whereby such a structure develops that the exchanger for the too adsorbent fabrics accessible remains.

Generally one manufactures fibers, filaments or foils after the invention process. Can with be rounded or profiled nozzle hole drillings, hollow

nozzles or slot nozzles be worked. The prefered solvent in the frame of the invention process is N-methylmorpholine-N-OXIDE-monohydrate.

15 The precipitated shaped bodies subsequent is given subsequent treatment to the removal of the amine oxide with water washed, and dried. The post treatment made convenient with suitable electrolytes, in order to regenerate the exchangable groups of the exchanger incorporated into the cellulose matrix.

By the Aufmahlung and dispersion of the ion exchangers in the extruding solution can become shaped bodies, in particular fibers, filaments or foils provided, which can exercise many different adsorbent functions in response of the exchangable groups of the ion exchanger.

So z can. B. by dispersion of a strong basic anion exchanger with quarternären ammonium groups into the active group CH n (CHc) Cl a shaped body generated become, which is suitable to the selective removal of nitrate ions from aqueous Mediums. If a weak basic ion
17 exchanger with primary amino group and an additional weak or strong acidic cation exchanger on the basis of polyacrylate or styrene sulfone acid becomes divinylbenzene in the sodium form into the cellulosischen shaped body introduced, then a filter z manufactured from this adsorbs. B. from cigarette flue gases on the one hand polar components, like the ciliarytoxic aldehydes (formaldehyde, acrolein, Crotonaldehyd, acetaldehyde and. A.) and the volatile phenols, and on the other hand the toxic basic smoke components, like ammonia, aromatic amines, hydrazine derivatives, as well as the toxic acidic smoke components, like prussic acid, nitric acid and. A.

As a result of dispersion of a weak acidic cation exchanger on Polyacrylharzbasis with carboxyl groups in the solution arise shaped bodies, which are suitable for the elimination of the temporary hardness and from heavy metal ions from water. Letzeres can do also very selective for series of Schwermetall-bzw. Transition metal ions by intercalation of weak acidic, chelatbildenden Iminodiacetatgruppen haltigen ion exchangers into the cellulose matrix take place.

Furthermore the object becomes dissolved by a composite, in particular as Tow, fleece, paper or felt, which exist at least partly out after the method of the claims 1 to 12 manufactured fibers. This composite can completely consist of manufactured according to invention
19 Lyocellfasern loaded with ion exchangers. The composite can insist also on basis of a mixture of cellulosischen fibers modified with different ion exchangers (cation exchangers and anion exchangers), whereby a composite with similar effects becomes obtained, as if a fibrous material with two or more different ion exchangers becomes loaded. Finally it is out according to invention also possible, a composite with ion exchangers loaded fibers as well as from normal Lyocellfasern or other fibers, like z. B. Polyethylene, polypropylene or pulp to manufacture in a NaBvliesprozess whereby one receives nonwoven fabrics with gradatable filter efficiencies. The bottom Tow specified above is to be understood a crimped sliver from many single filaments.

The composite according to invention is suitable for the use as filter material for the removal of ions and polar compounds from solutions, gases and steam. The operating range covers in particular filters for cigarettes, household machines etc. for the removal of toxic or disturbing inorganic or organic ions and molecules, like z. B.

21 Nitrate, Nitrit-und Bicarbonatanionen, heavy metal cations, acidic or basic organic compounds, polar organic compounds, like aldehydes and Ketonen. The center of gravity lies differently than with the filter after WHERE 95/35044 in the adsorption of molecular-disperse, in particular toxic components, which do not ten by exchanger-free Lyocellfasern zurückgehal become. Used the according to invention ion exchangers are solid substances, which do not become in the cellulose matrix only incorporated, however dissolved. Therefore none exist by the solubility in Spinn and/or for these ion exchangers mix-mA-bend. Extruding solution predetermined quantitative limitations.

For the other clarity of the invention process and the characteristics relevant for the use of the procedure products the subsequent examples serve.

Example 1
9 mass % igen cellulose solution in N-methylmorpholine-N-OXIDE-monohydrate becomes a powdery nitrate-selective strong basic anion
23 exchanger on that
Basis macroporous styrene Divinylbenzol-copolymer with tri alkyl ammonium
Groups in chloride form and a grain size < 15 pm in a weight of
100 mass %, related to the cellulose portion, added. This Spinnlösung becomes in a kneader homogenized and with a temperature of approx. 90 C by one
Spinneret with 150 hole spun. The departure speed amounts to 20 m/min.

The multi-file thread becomes by several wash baths guided, around the N
to remove Methylmorpholin N oxide. Afterwards the thread becomes by a one percent aqueous Kochsatztösung guided, around the chloride form of the incorporated Ionenaus to generate diver material complete. The thread becomes ge in stacks of 6 mm cut, with approx. 80 C dried or centrifuge-humid leave. The fibers have a titre of 1,78 tex, an elongation of 21,1% and a tearing strength of 11,6 cN/tex. The total capacity according to DIN 54402 in aqueous solution amounts to 1.3 mmol/g
Fiber.

25 It became the rate of the adsorption of nitrate ions from more aqueous
Solution bottom use of the obtained fibers as adsorbent certain.

The comparison the adsorption of the nitrate ions became from the same solution with in this example used anion exchanger, however in Perl form with an effective grain size k 430 pm and a mean grain size from 600 to 800 around conducted. The fig shows the different Adsorption speeds of the perlförmigen ion exchangers and invention in accordance with manufactured ion exchanger fibers.

Example 2 Cellulosemai N-methylmorpholine-N-oxide aqueous in 60%-igem becomes an aqueous suspension of a strong basic anion exchanger on the basis gelförmigen styrene Divinylbenzol-copolymer with tri alkyl ammonium groups in chloride form and a weak acidic,
27 macroporous Kationentauschers on the basis styrene Divinylbenzol-copolymer with chelatbildenden Iminodiessigsäure groups in such a concentration added that the Spinnlösung contains 9 measures % cellulose and related to this cellulose quantity of 99 mass % Anionentau and 1 mass % Kationentau. The grain size of the suspended is more Ionentauscher < 15 over. After the Abdestillieren of the water up to the NMethylmorpholin N OXIDE monohydrate and dissolving the cellulose the Spinnlösung becomes after example 1 versponnen. The fibers have a titre of 1,27 tex, an elongation of 24,8% and a tearing strength of 9,9 cN/tex. The total capacity according to DIN 54402 in aqueous solution amounts to 1.3 mmol/g fiber. Additional ones become selective heavy metal ions such as z. B. Copper and lead with a capacity of 0,01 mmol/g fiber bonded.

Example 3 Cellulosemai in 60%-igem N-methylmorpholine-N-oxide becomes an aqueous suspension of a weak acidic macroporous Kationentauschers on the basis of crosslinked polyacrylate in the sodium form in such a concentration added that the Spinnlösung 10 contains mass % cellulose and related to the cellulose portion of 70 mass % of the Kationentauschers. The grain size of the suspended Ionentauschers was attached < 15 pm. After the Abdestillieren of the water up to the NMMNO monohydrate and the resolution of the cellulose the Spinnlösung becomes after example 1 versponnen. After washing N-methylmorpholine-N-oxide the made regeneration of the sodium form of the Kationentauschers into the H+-form with diluted sulfuric acid. The thread becomes cut in stacks of 6 mm, with approx. 80 C dried or centrifuge-humid leave. The fibers have a titre of 1,45 tex, an elongation of 25% and a tearing strength of 7,65 cN/tex. Lo

nentauscherfasern possess a total capacity according to DIN 54402 of 4,3 mmol/g fiber in aqueous solution.

Example 4 Spinnlösung manufactured after example 1, becomes with a temperature of approx. 90 C by a slot nozzle to a foil with a thickness of approx. 40 pm in the dried state deformed. The nozzle slot had a length of 62.8 mm and the distance of the nozzle to the aqueous drop bath amounted to 10 mm. The foil outgoing from the nozzle became after the clearance by 2 water baths of 6 m length guided and wound. The drying process of the foil made with 60 C. The total capacity of this foil was to foil at 1,25 mmol/g.

29 Example 5 9 cellulose solution in N-methylmorpholine-N-OXIDE-monohydrate becomes a powdery weak basic Anionentau styrene Divinylbenzol-copolymer with primary amino group and a grain size, macroporous on the basis, mass % igen < 15 pm in a weight of 60 mass % related to the cellulose portion added. This Spinnlösung becomes in a kneader homogenized and with a temperature of approx.

90 C by a spinneret with 150 hole spun. The departure speed amounts to 20 m/min. The multi-file thread will by several wash baths guided, in order to remove the N-methylmorpholine-N-oxide. The thread is left in stacks by 6 mm of cut and centrifuge-humid. The fibers have a titre of 1,0 tex, an elongation of 21% and a Reil3kraft of 17,0 cN/tex. This fiber becomes with 25% of a fibrillated Lyocellfaser with a titre of 1,7 dtex and 25% of a fiber from example 3 mixed and in a Nassvtiesantage a fleece with a basis weight of 30 g/m2 processed. Filter attempts with this fleece at cigarette smoke a shown filter efficiency for entire-volatile aldehydes of 51%, for hydrogen cyanides of 70% and for ammonia of 65%.

31 Example 6
9 mass % igen cellulose solution in N-methylmorpholine-N-OXIDE-monohydrate becomes powdery weak basic Anionentau on the basis of a macroporous Styrene Divinylbenzol-copolymer with primary amino group and a grain size < 15 over in a weight of 100 mass %, related to the cellulose portion, added.

This Spinnlösung becomes in a kneader homogenized and with a temperature of approx.

90 C by a spinneret with 150 hole spun. The departure speed amounts to
33 20 m/min. The multi-file thread becomes by several wash baths guided, around that
to remove N-methylmorpholine-N-oxide. The thread is left in stacks by 6 mm of cut and centrifuge-humid. The fibers have a titre of 1,1 tex, an elongation of 23% and a tearing strength of 12,5 cN/tex. This fiber becomes same parts with egg more ner fibrillated Lyocellfaser with a titre of 1,7 dtex and same pile-prolonged ge mixes and in a Nassvtiesantage a fleece with a basis weight of 30 g/m2 processed. This fleece has a total capacity according to DIN 54402 in aqueous solution of
1,0 mmol/g fleece. Filter attempts with this fleece at cigarette smoke of shown filter efficiency for entire-volatile aldehydes of 72% and for hydrogen cyanide of 55%.